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Mechanical and Thermal Properties of Polyamide 6/HDPE-g-MAH/High Density Polyethylene

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Abstract

Blending of polyamide 6/high density polyethylene (PA6/HDPE=70/30 wt%) was prepared by melt compounding using a twin screw extruder followed by injection molding using HDPE-g-MAH served as compatibilizer. A series combination of PA6/HDPE with HDPE-g-MAH were blended with varied composition of 100/0, 98/2, 96/4, 94/6 and 92/8. The mechanical properties of the samples such as tensile test, flexural test and elongation at break were measured by universal tensile machine while hardness was measured using the Zwick Roell hardness tester. The composites were characterized by Fourier Transform Infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and Thermogravimetric Analyzer (TGA). The addition of HDPE-g-MAH (2wt%) showed increased in modulus, strength and hardness but elongation at break decreased. DSC tests showed similar trend for all compositions. All mechanical tests also showed that composition of 98% PA6/HDPE with 2% HDPE-g-MAH has the highest value indicated best formulation for this research.

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Keywords: Polymer blend; polyamide 6; HDPE; HDPE-g-MAH; compatibilizer; mechanical properties; thermal characterization

1. Introduction

Polymer blends and composites are a part of everyday used and become more popular in an engineering industry because it possesses high tensile and impact strength. Polyamide 6 (PA6) has an excellent properties such as hydrogen bone in molecular chains of the polyamide which makes it one of the major engineering and high performance plastic. A new component in blends with other polymers can improve the performance by both blending and adding nanoparticles. The research on multicomponent of polar and nonpolar polymer materials has emphasized in the development of nanocomposite. Modified of nanocomposite has attached much attention for the last 13 years [1]. Conventionally combination of PA6 and HDPE are immiscible, so compatibilizer has been used to reduce interfacial energy between two polymer blend to increase adhesion. There are many types of compatibilizer that have been studied by researchers such as ethylene vinyl acetate (EVA) [2], SEBS-g-MA [3], PE-g-MAH [4] , LDPE-g-MAH [5], HDPE-*grafted*-acrylic acid (PEAA) [6]and banana fiber (BaF) [7].

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Tjong *et al.,* [3] reported that additional of 10 wt% SEBS-g-MA caused a double increase in the impact fracture toughness of HDPE/2 wt% Org-MMT and HDPE/4 wt%/Org-MMT nanocomposites. The high polarity of the MA group allowed SEBS-g-MA improves compatibility among the filler and polymer. Most of platelets were concentrated in the PA6 phase and interfacial region among PA6/HDPE (PEAA) played the role of coupling species among the two polymers, increasing the interaction of the two phases in certain extent. Recently, Liu *et al.,* [7] have been investigating the effect of two different compatibilizers to the properties of banana fiber (BaF) composites based on HDPE/PA6 blend. Better strengths and modulus were found for HDPE/PA6 based composites in the presence of males anhydrate grafted SEBS-g-MA compares with equivalent HDPE composites. Besides that, by increasing BaF loading up to 48.2 wt% led to successive improvement in modulus and flexural strength but the impact toughness was reduced in stage.

In 2008, Kusmono [8] reported that ductility, impact strength and fracture toughness was increased by addition of SEBS-g-MA into PA6/PP/organoclay nanocomposite. By contrast, the tensile strength of PA6/PP was decrease by 11 wt% in the presence of 5 phr SEBS-g-MA. This is due to the chemical reaction among maleic anhydride group, SEBS-g-MA and the amine group, PA6 lead to locate at the blend interface then has a tendency to decrease the concentrations around the disperse particle. Available investigation showed that addition of SEBS-g-MA in PA66 matrix cause impact strength and elongation at break increase but slightly decrease tensile modulus, tensile strength and hardness of the matrix [9]. However, little work has been done on PA6/HDPE with the presence of compatibilizer, HDPE-g-MAH to achieve a good balance of polymer blend. The investigation of the mechanical properties and characterization of PA6/HDPE with HDPE-g-MAH as compatibilizer are reported.

2. Experimental

1.1 Materials

Polyamide 6 (Amilan CM 10170) was obtained commercially from local company. The melt flow index and the density of PA6 were 35g/10 min and 1.14g/cm^3 at 230°C and 2.16 kg. HDPE (5740UA) with the melt flow index of 4 g/10min and a density of 9.57 g/cm^3 were also supplied by local company, Malaysia. The Maleic Anhydrate Grafted Polyethylene (MAPE) or HDPE-g-MAH used in this study was DuPont Fusabond E MB100DH obtained in pellet shape with a density of 1.36 g/cm^3.

1.2 Sample preparation

PA6 was dried at 80°C for 16 hours before blend to remove moisture content. PA6 and HDPE were dry mixed by shaking manually then consolidated with HDPE-g-MAH before feeding into the extruder. Twin-screw extruder (model Haake Rheomex OS, PTW16) with the barrel temperature kept at 190-230°C and screw speed of 70 rpm was used. This procedure was repeated for PA6/HDPE (100, 98, 96, 94 and 92) wt% mixed with HDPE-g-MAH (0, 2, 4, 6 and 8) wt %. All the extrude samples were kept cool before cut (pallet form) using palletizer and placed in desiccators to avoid any moisture defect. Samples in pallets then were dry again before being injected to obtain dumbbell-shaped tensile bar using injection molding machine model HWT GLOTECH (VDCII-140). The typical operating conditions, barrel temperature were set at 200, 210, 220, 230 and 240 °C respectively, mean residence time was 2 min, mold pressure is 70 bars and mold temperature was 50 °C.

1.3 *Mechanical testing*

Tensile properties such as modulus, tensile strength and elongation at break were measured using a tensile machine (INSTRON 3382) involved extensometer at a room temperature with a crosshead speed of 50 mm/min. Flexural modulus and strength were determined using the same tensile machine with a 64 mm support span at a crosshead speed of 3 mm/min. Hardness test was measured using Rockwell hardness tester (model A654 R). All these tests were repeated for five cycles in each experiment**.**

1.4 Thermal characterization

Thermal properties were characterized by differential scanning calorimeter (DSC) to study the melting behavior using METTLER TOLEDO in nitrogen atmosphere. The samples were scanned at a heating rate of 10 °C/min and heated from room temperature to 300 °C, held at this temperature for 5 minutes to erase the thermal history during processing. The value of the melting temperature (T_m) was obtained respectively. Thermal stability of the samples was characterized using a thermogravimetric analyzer (TGA/SDTA 851) with the heating rate of 10 °C/min under nitrogen atmosphere at a flow rate of 60 ml/min.

1.1. FTIR analysis

The Fourier Transformation Infra-red (FTIR) spectrum test were performed on a Perkin Elmer precisely at a resolution of 4 cm^{-1} and scans over the range wave number of 550-4000 cm^{-1}. Prior to scanning, the samples of the blends were compressed molded with ~0.1 mm into film. Then, the sample was cooled at the room temperature.

2. Results and discussion

2.1. Mechanical properties

Based on the procedure described in the previous section, PA6/HDPE blends containing 0, 2, 4, 6 and 8 wt% of HDPE-g-MAH have been prepared in ratio 98/2 wt %. The effect of HDPE-g-MAH on the tensile modulus (TM), tensile strength (TS), elongation at break (EB), flexural modulus (FM) and flexural strength (FS) of the samples are summarized in Table 1. The results show that tensile modulus increased by addition of HDPE-g-MAH but decreased by incorporation of more than 2 wt% of HDPE-g-MAH in the blends. The result also revealed that tensile strength was increased with the increasing of HDPE-g-MAH content up to 2 wt%. This means, 2 wt% of compatibilizer was enough to link the polar polymer (PA6) with the HDPE in the blends and eventually lead to improve the structure. However, addition of excess compatibilizer has a high potential to drag the structure gradually weakening in the blends then decreased tensile strength.

Table 1. Mechanical properties of the blends on the tensile modulus (TM), tensile strength (TS), elongation at break (EB), flexural modulus (FM) and flexural strength (FS).

Designation		TM (MPa)	TS (MPa)	EB (%)	FM (MPa)	FS (MPa)
PA6		2746.5	68.38	2.45	2153.59	89.21
HDPE		1071.8	22.44	21.10	643.01	20.01
HDPE-g-MAH		1003.9	24.17	18.66	726.353	22.78
PA6/HDPE (wt%)	HDPE-g-MAH (wt%)					
100	0	1595.8	34.75	7.98	1399.31	48.39
98	2	1828.2	44.81	2.20	1701.75	58.71
96	4	1519.8	36.11	8.91	1542.50	53.20
94	6	1480.0	34.60	17.51	1497.00	49.29
92	8	1387.7	34.39	26.39	1354.63	41.68

According to Kusmono *et al*., (2008), Dermanakifarahani (2008) and Tang *et al*., (2007) the elastomeric nature of the compatibilizer significantly caused this situation to happen [8, 10]. Flexural modulus and flexural strength were also increased up to 2 wt % of HDPE-g-MAH then slightly continued to decrease until addition of 8 wt% of HDPE-g-MAH. Incorporation of HDPE-g-MAH (2 wt%) improved interfacial adhesion between PA6 and HDPE as PA6-g-HDPE copolymer was formed during blending and thereby resulted in a better and finer dispersed phase. At

the same time, interfacial tension rapidly decreases. A similar behavior was reported by Farahani [9] for SEBS-g-MAH and Mat Uzir [11] for PPgMAH. According to Dayma *et al*. [12] yield strength was decreased due to improvement of the plasticization effect of the low weight PP-g-MA when it only acts as compatibilizer in a certain condition. Addition of HDPE-g-MAH in the blends may cause PA6/HDPE to become well-mixed by increasing the ultimate strength as compatibilizer induce an important role in controlling tensile and flexural properties [13].

The Zwick Roell hardness test results of the blends were given in Fig. 1. The result shows hardness for blend unfilled HDPE-g-MAH is about 69.4 and the value was increased after addition of 2 wt% of HDPE-g-MAH. Nevertheless, further addition of HDPE-g-MAH resulted decrease hardness until constant value with 70. Incorporation of HDPE-g-MAH into blending improved in hardness as interfacial adhesion in the blends increases. But the addition of excess HDPE-g-MAH correlated to lower hardness because the structure was not stable enough since hardness values depend on the modulus of the polymer. A similar observation was noted by Karsli and Aytac also Chong *et al.* [14, 15], noted that hardness was lower with more HDPE in polymer blend as the result accorded with the addition principle of the properties for a polymer alloy.

2.2. Thermal properties

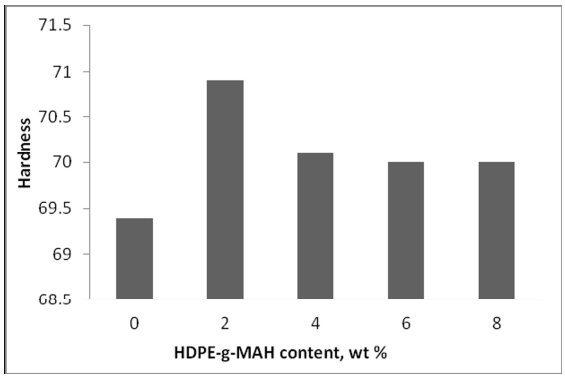

Fig. 1. Hardness test for different composition of HDPE-g-MAH

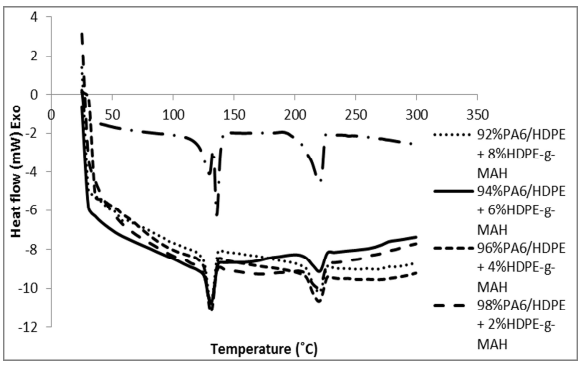

Fig. 2. DSC heating thermograms of PA6/HDPE blends in different composition of HDPE-g-MAH compatibilizer

Fig. 2 illustrates the DSC heating thermograms of PA6/HDPE with and without HDPE-g-MAH compatibilizer under the heating rate of 10 ˚C/min and nitrogen flow rate at 35 ml/min. Moreover, melting temperature for all studied blend is listed in Table 2. From Fig. 2, apparently all samples demonstrated two strong melting peaks (130-136˚C and 220-221˚C). The melting peak about 130-136˚C and 220-221˚C correspond to the melting temperature (T_m) of HDPE and PA6 respectively. Here, PA6/HDPE blend achieves the higher melting temperature of HDPE before slightly decrease after addition of HDPE-g-MAH. This result is due to the low crosslinking density of the polymer blends and agreed to the result obtained by Chong *et al.* [14] for PA46/HDPE polyblends. Incorporation of maleic anhydride in the presence of HDPE-g-MAH did not produce any much significant changes in the melting temperature of PA6. Referring to Jose *et al.,* the existence of SEBS-g-MA in the PA6/PP blend caused the interfacial chemical reaction between maleic anhydride, SEBS-g-MAH and amide group, PA12 occurs in the amorphous phase, therefore did not contribute appreciable change in melting behaviors [16]. Furthermore, this result proved that blending process not easily made the polymer lost its original properties.

Table 2. DSC result for PA6/HDPE blends with a several composition

Blending composition	PA6 T_m (°C)	HDPE T_m (°C)	$T_{d\,(5\%)}$ (°C)	$T_{d(50\%)}$ (°C)
PA6/HDPE	220.65	136.54	410.90	452.10
PA6/HDPE/ 2 wt% HDPE-g-MAH	220.63	130.61	411.11	452.63
PA6/HDPE/ 4wt% HDPE-g-MAH	221.84	130.61	412.77	452.88
PA6/HDPE/ 6 wt% HDPE-g-MAH	220.34	130.46	407.67	452.25
PA6/HDPE/ 8 wt% HDPE-g-MAH	221.61	130.54	407.36	425.47

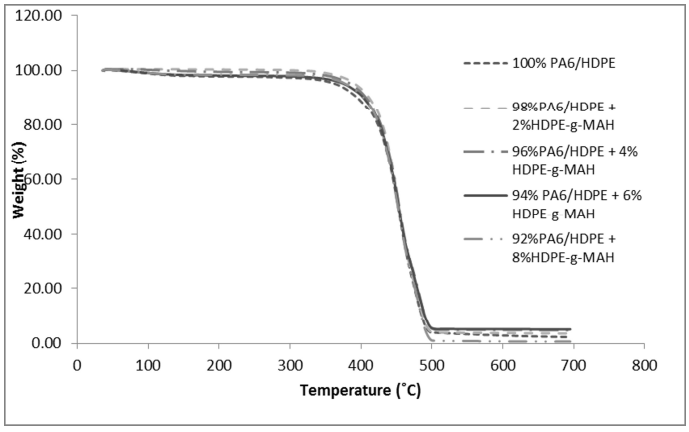

Fig. 3. TGA curve of PA6/HDPE blends in different composition of HDPE-g-MAH compatibilizer

The thermogravimetric analysis (TGA) was conducted to understand the thermal behavior of the sample the curves are shown in Fig. 3. According to Kusmono *et al.,* [8] the onset decomposition temperature was characterized by the temperature at 5% weight loss ($T_{5\%}$) and the data are listed in Table 2. As can be seen, decomposition of PA6/HDPE without compatibilizer start at 410.9˚C and while the onset decomposition of PA6/HDPE/2%HDPE-g-MAH was observed at 411.11˚C. This result significantly revealed that addition of HDPE-g-MAH in the PA6/HDPE blend lead to increase the thermal degradation and shift to higher temperature at the beginning stage. Even so, the addition of more HDPE-g-MAH attributed the thermal stability decrease significantly. Thus, it clearly depicted that presents of compatibilizer at certain composition (2%HDPE-g-MAH) enhance the thermal stability of the polymer. Overall, even though thermal stabilities were increase at first then slightly decrease by increasing in temperature but all samples still exhibited almost the same trend.

2.3. FTIR Spectra

FTIR tests were run (550-4000cm^{-1}) for all blended samples to track the presence of functional group in each sample. Fig. 4 shows the FTIR spectra of the different composition blending started from the pure material until the addition of HDPE-g-MAH compatibilizer. Based on Fig. 4, all samples shown the existence of alkyl groups, C-H stretches at bands in the range of 2915-2935 cm^{-1}. PA6 show bands of ester group, C=O unsymmetrical stretching of the imide group at 1738 cm^{-1}, amide I (C=O stretching) at 1637cm^{-1}, and amide II, N-H bonding + C-N stretching. PA6/HDPE sample shows a N-H stretching (3289 cm^{-1}), C-H stretching (2915 cm^{-1}), C=O stretching of imide group (1740 cm^{-1}), C=O stretching of amide I (1633 cm^{-1}) and N-H bonding + C-N stretching of amide II (1533 cm^{-1}). Several interfacial reactions would occur on PA6/HDPE/HDPE-g-MAH during blending section such as

decomposition of MA group and interaction among main chains HDPE-g-MAH, HDPE and functional group of PA6 [8]. Sample with HDPE-g-MAH compatibilizer shows almost the same peak as PA6/HDPE, no new absorption peak is demonstrates but no ester group appears in this band. According to Tjong and Bao [3], these phenomena attributed that MAH group grafted degrade into –COOH during melting process. Thus, the reaction of PA6 on amine group, HDPE on alkyl group and maleic anhydride on HDPE-g-MAH form a PA6-g-HDPE copolymer presented. This formation is proved by the presence of an overlapped functional group of C-H and N-H in the graph.

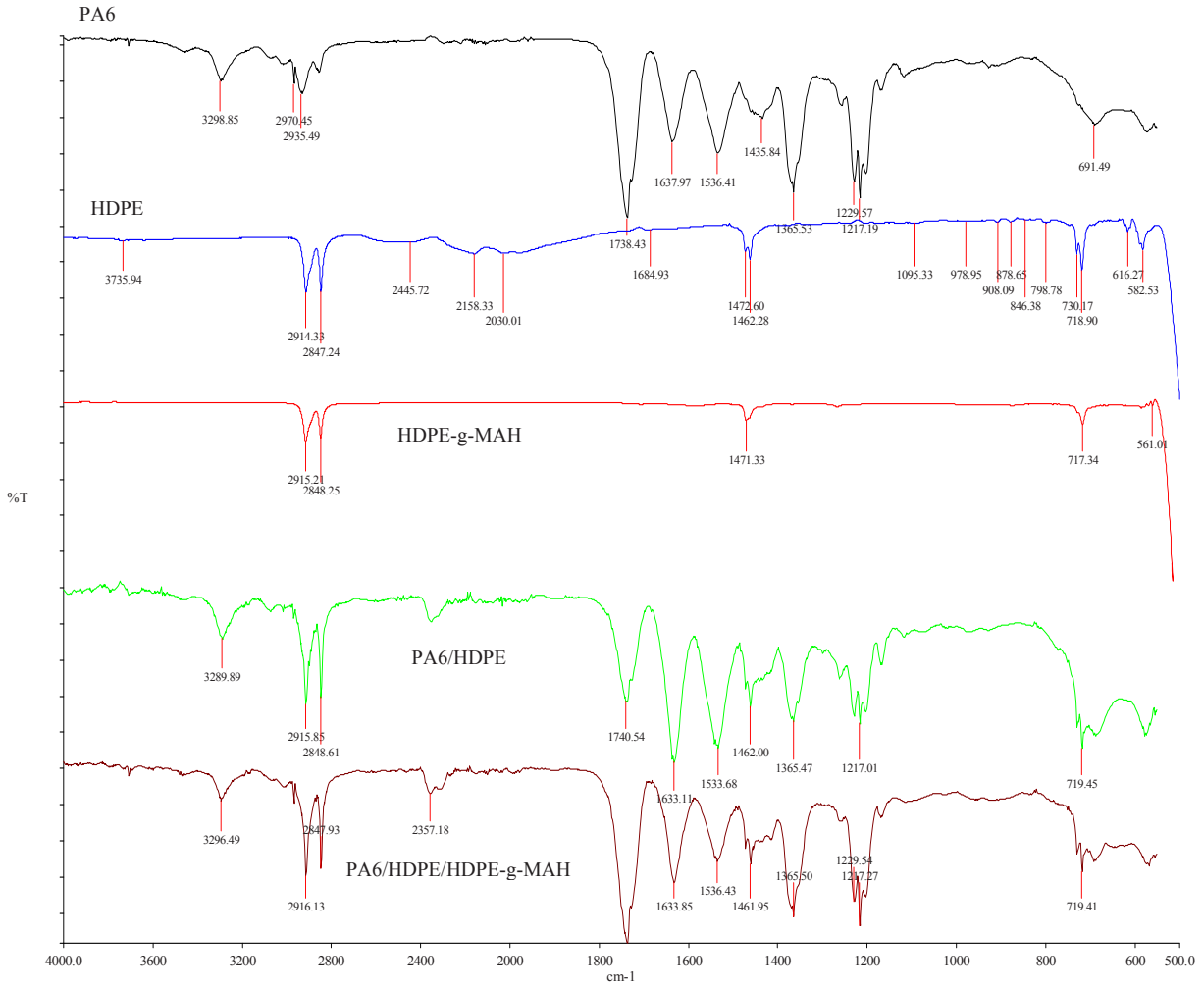

Fig.4. FTIR spectra of PA6, HDPE, HDPE-g-MAH and blending sample

3. Conclusion

As a conclusion, the mechanical properties of Polyamide 6/High Density Polyethylene (PA6/HDPE=70/30) blend matrix without several compositions of HDPE-g-MAH was evaluated. The results revealed that tensile strength increased with the increased in HDPE-g-MAH content up to 2 wt%. However, tensile modulus and hardness decreased by increasing the amount of HDPE-g-MAH. Flexural modulus and flexural strength also increased up to 2 wt % of HDPE-g-MAH then slightly decreased until addition of 8 wt% of HDPE-g-MAH because the addition of excess compatibilizer has a high potential to drag the structure gradually weakening. Incorporation of HDPE-g-

MAH (2 wt%) improved interfacial adhesion among PA6 and HDPE as PA6-g-HDPE copolymer. The DSC / TGA showed that the thermal stability of the PA6/HDPE improved after the inclusion of 2-4% of HDPE-g-MAH. 98% PA6/HDPE with 2% HDPE-g-MAH showed the highest value of mechanical properties.

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